A SHOCK TUBE TECHNIQUE FOR STUDYING THE KINETICS OF HIGHLY EXOTHERMIC REACTIONS---SHOCK INITIATED DETONATIONS.

Roger A. Strehlow*
Aeronautical Engineering Department
University of Illinois
Urbana, Illinois

and

Arthur Cohen
Ballistics Research Laboratories
Aberdeen Proving Ground, Maryland

INTRODUCTION

The incident shock techniques which are so well adapted to the study of endothermic reactions[1], are in general, not applicable to the study of highly exothermic reactions. This is because an exothermic reaction occurring in a small region of a flowing gas causes an increase of the local pressure and in the case of shock wave heating this pressure increase occurs behind and close to the shock front. Since this region is subsonic the pressure increase will propagate as a wave to the front and increase the velocity of the front, thereby increasing the temperature of the next element of gas heated by shock compression. This process is self accelerating and in general a steady state wave will not be obtained until the wave is traveling at or above the Chapman-Jouget detonation velocity for the mixture. Since in all reaction kinetics work one must follow the history of a fixed element of gas, incident techniques will only work if the wave is truly steady state in time. Therefore highly exothermic systems may be studied by incident techniques only in the limit as steady detonation waves.

In the endothermic case the reaction locally lowers the pressure behind the shock wave thereby slightly lowering shock velocity. A steady shock wave followed by a reaction wave can therefore be generated and studied. Schott and Kinsey[2] have demonstrated that steady waves can also be generated and studied in weakly exothermic mixtures.

A different situation exists for the region behind a reflected shock. Here the gas is essentially quiescent at the back wall and fixed station observations should yield meaningful results. Furthermore the reflected shock provides nicely controllable initial conditions for observing the details of the accelerating process.

---

*On leave from the Ballistics Research Laboratories as a Ford Foundation Visiting Professor.

Recently, we observed that a highly exothermic reaction occurring behind the reflected shock can quite reproducibly generate one dimensional accelerating waves that are either: 1) "detonation" waves which eventually overtake and interact with the reflected shock wave, or, 2) pressure waves which cause a simple acceleration of the reflected shock.[3] This paper describes our conclusions concerning design limitations for the reflected shock technique, some of our further observations of the acceleration phenomena in the hydrogen-oxygen system, and our observations of adiabatic explosion delays in hydrogen-oxygen mixtures.

DESIGN LIMITATIONS

The step reflected shock produced at the end of a conventional shock tube is, within certain limitations, well suited for the study of highly exothermic reactions. These limitations are:

1. Reflected shock heating is clean (i.e. truly one dimensional) only if the heat capacity ratio of the gas mixture is greater than 1.4 over the temperature range used in the experiment.[4]

2. Only reactions which occur rapidly at high temperatures may be studied. Only at the higher temperatures is the reflected shock temperature sufficiently above the shock temperature to allow rapid reaction in this region with no earlier reaction behind the incident shock.[4] A rapid reaction is defined here as one in which the events of interest occur in the time range 10 to 1000 microseconds.

3. The explosive mixture must be separated from the diaphragm by an inert gas mixture of similar properties (buffer gas) and the interface between the two gases must not generate reflected shocks when the incident shock traverses the boundary. Once again local reflected shocks in the explosive mixture could trigger early detonation.[5]

4. Small cracks and crevices in the tube wall must be entirely absent. These produce local reflected shock waves which could trigger early detonation.[6]

5. In general the reflected shock is not as ideal as the incident shock wave.[4,7] In pure argon the best current estimate is that the reflected shock gas temperature is approximately 30^{o} to 50^{o} below theoretical in the range $1500^{o}K < T_{rs} < 3000^{o}K$.

EXPERIMENTAL

A four inch i.d. stainless steel shock tube with a 50 inch compression section, an 88 inch buffer section and a 164 inch test section was used in these experiments. The buffer section was separated from the test section by a four inch stainless steel ball valve (a six and one half inch sphere with a four

inch hole bored through it) which allowed undisturbed passage of the shock when in the open position. When closed the valve was vacuum tight and allowed us to place an inert gas, of the same density as the explosive gas, in the section near the diaphragm and in the bore of the valve. Pressure differential across the valve was adjusted to zero externally and the valve was opened about 10-20 seconds before firing the tube. This effectively prevented any premature detonations initiated by non-ideal diaphragm burst. Also, the test section was constructed to eliminate all internal crevices at the joints and window mountings in order to eliminate premature detonations caused by local reflected shocks. Strip photographs (x-t) of reflected shock behavior were taken with an eight inch schlieren system through 8" X 0.025" slit windows at the back wall. Other experimental details are given in a previous paper.(4)

One dimensional steady state shock wave and detonation calculations were performed on the Ballistic Research Laboratories' high speed computer, the EDVAC. Thermodynamic data for the gases was taken from recent Bureau of Standards tables. Shock calculations were performed with the assumption of no reaction or dissociation but rapid vibrational relaxation in the shock. Detonation calculations were performed by assuming complete thermodynamic equilibrium in the wave. The C-J velocity was calculated using the frozen equilibrium velocity of sound.

RESULTS

Schlieren strip film (x-t) photographs of the reflected shock region were taken in stoichiometric hydrogen-oxygen mixtures diluted with 70%, 85% and 94% argon. In the range $2.14 < M_s < 2.8$ ($920^{\circ}K < T_{rs} < 1820^{\circ}K$) reaction was evident behind the reflected shock. All our photographs indicated that the initial reaction was typical of a homogeneous adiabatic explosion with a finite delay. Delays ranged from 12 to 880 microseconds. In addition we observed that the wave nature of the heating cycle produced a reaction wave which traveled away from the back wall at or above the reflected shock velocity.

Two types of accelerating wave behavior were observed in hydrogen-oxygen-argon mixtures. Figure 1 illustrates the case where the reaction generates a weak pressure wave which travels to the reflected shock causing it to accelerate to a new steady velocity. During this process the reaction zone also accelerates and eventually reaches a new position closer to the reflected shock wave. Figure 2 is typical of the other type of behavior observed. Here the pressure wave steepens into a shock wave before it reaches the reflected shock. This reaction shock is followed by a narrow dark zone (i.e. no gradients) and then a strong rarefaction wave (gradients opposite to that in the shock). This wave pattern accelerates and grows more compact as it travels away from the back wall of the tube and finally interacts with the reflected shock, producing a new high strength shock (now closely followed by the rarefaction zone). The interaction with the reflected shock also produces a contact discontinuity which is traveling away from the back wall initially but quickly decelerates to zero

velocity and a sometimes observed weak rarefaction wave which travels toward the back wall of the shock tube at a constant velocity. The shock-rarefaction pattern which we observe, both before and after interaction with the reflected shock wave, suggests a detonation wave. The steady velocity of this wave in the incident gas agrees well with C-J calculations. However, wave velocities measured ahead of the interaction show that these accelerating waves are traveling at approximately one half the C-J velocity for this region. It is interesting that this non-steady wave has never exhibited any of the characteristics of spinning detonation. Occasionally we have observed slightly non-one-dimensional behavior at the start of wave formation but in every case these non-idealities were rapidly damped and the wave quickly became a strictly one dimensional wave perpendicular to the wall of the four inch shock tube.

In all cases where reaction was observed behind the reflected shock wave the delay to adiabatic explosion at the back wall was measured by extrapolating the wave motions to the back wall. These delays are compared to Schott and Kinsey's[2] recent data in Figure 3. Their data line represents the delay to the first appearance of OH radicals in absorption while ours represents the delay to the actual adiabatic explosion. Dr. Schott has indicated in a private communication that their delays to maximum OH concentration were about one and one-half times longer than their appearance delays. Our delays are, on the average, 1.2 to 2.0 times longer than Schott and Kinsey's delays. This indicates that at the back wall we are indeed observing an exothermic reaction under well controllable and calculable conditions free from the complications of the acceleration process.

THE MECHANISM OF DETONATION INITIATION

In the "detonation" case described above it is obvious that we are dealing with a very special and interesting case of detonation initiation. It is an interesting case because it is so nicely one dimensional and reproducible. It is special because the wave that is generated behind the reflected shock has all the gross characteristics of a detonation but travels at approximately half the calculated C-J velocity.

The qualitative behavior of this wave system may be described if we first make some assumptions concerning the reaction and then mentally remove them one at a time. Let us assume that: 1) the reaction starts after a finite delay time τ which is constant for every element of gas, 2) the reaction rate is infinite (i.e. $t < \tau$, no reaction; $t > \tau$, complete equilibrium), 3) no heat evolution or molecular weight change occurs during the reaction. With the above assumptions the reaction would appear as a reaction wave traveling at the same velocity as the reflected shock. In Figure 4 the dotted line $(RW)_o$ represents this situation. If we remove condition three and allow the reaction to liberate a quantity of heat, the reaction wave will separate regions of low and high temperature. The continuity equations of gas dynamics predict that for this simple situation you will observe a centered wave pattern consisting of a shock wave (reaction shock) followed by

the reaction wave (RW). These waves separate steady state regions and the shock strength is determined by the exothermicity of the reaction and the added condition that the particle velocity be equal to zero at the back wall. The shock which is produced is identical to that obtained with a piston motion drawn as the equivalent piston path in Figure 4. The light lines represent a particle path through the idealized centered wave pattern.

Removing assumption number two and allowing finite reaction rates will cause the shock wave to appear some distance from the back wall. This is equivalent to a slow acceleration of the piston instead of the impulsive motion illustrated in Figure 4, and it causes the wave to accelerate near the region of wave formation. This acceleration will lead to a terminal shock velocity which can be calculated from the equilibrium properties of the gas and the reflected shock strength. Removal of assumption number two therefore allows one to predict that an approximately centered constant velocity expanding wave pattern will appear some distance from the back wall. A close look at this wave pattern shows that assumption number one (constant τ) becomes less and less valid as the pattern expands. Heating by the reaction shock soon causes an appreciable decrease in the delay and the wave system becomes self accelerating. One additional feature, the observed rarefaction wave, is undoubtably produced because the gas leaving the accelerated reaction wave has a net velocity away from the back wall and must therefore be decelerated to zero velocity.

The intersection of the accelerating wave pattern and the reflected shock produces the interaction described in the results section. This behavior is adequately predicted by one dimensional gas dynamics. A momentum balance on this interaction shows that the forward traveling resultant shock will be moving faster than the calculated CJ velocity for this region. One would therefore expect the resultant wave to decelerate to the velocity of a high order detonation. This is what is observed experimentally.

SUMMARY AND CONCLUSIONS

Reaction mechanisms may be studied using a reflected shock technique even for the case of highly exothermic reactions. Fixed station observations near the back wall will allow the study of chemical species for the case of homogeneous adiabatic explosions. Furthermore, if the range of reaction time and the geometry of the system is carefully chosen one should be able to study the reaction without the bothersome influence of wall effects. The time history of the explosion will be slightly different than in a closed vessel: first because the reaction will in general be truly homogeneous, and second, because the gas dynamics allows the volume of the "vessel" to increase during reaction. The application of this technique should allow the direct study of the details of many exothermic reactions in the temperature range of current interest (i.e. flame temperatures).

The accelerating waves observed during our investigation are even more interesting. We observe a wave pattern reminiscent of a

detonation under conditions where the "reaction wave" is passed through a combustible mixture at an arbitrary velocity determined by the reflected shock velocity. (This arbitrary velocity is much higher than the normal flame propagation velocity for these mixtures.) The general features of this wave pattern can be explained qualitatively using one dimensional gas dynamics with heat addition. An exact treatment of the wave development will require the use of the method of characteristics and a knowledge of the rate of heat release in the reaction zone and the effect of shock heating on the delay time

From the brief analysis given above it is evident that these nicely one dimensional accelerating waves are "uncoupled" or "weakly coupled" when first produced. That is, the reaction wave is physically well removed from the shock wave. Hirschfelder and Curtiss[8] have recently discussed the "coupling" of the shock wave and reaction zone in steady detonation waves. A detailed study of this initiation process for a variety of exothermic reactions should yield a great deal of information on the structure of stable detonation waves for specific explosive mixtures.

REFERENCES

1. H. Pritchard, Quarterly Reviews, 14, 46-61, 1960;
   A. Hertzberg, Appl. Mech. Rev., 9, 505, (1960);
   T. Carrington and N. Davidson, J. Phys. Chem., 57, 418, (1953).

2. G. Schott and J. Kinsey, J. Chem. Phys., 29, 1177-82, (1958).

3. R. Strehlow and A. Cohen, Phys. of Fluids, 3, 320, (1960).

4. R. Strehlow and A. Cohen, J. Chem. Phys., 30, 257-65, (1959).

5. J. Fay, Some Experiments on the Initiation of Detonation in $2H_2 - O_2$ Mixtures by Uniform Shock Waves, 4th Symposium (International) on Combustion, 501-7, Williams and Wilkens, Baltimore (1953).

6. M. Steinberg and W. Kaskan, The Ignition of Combustible Mixtures by Shock Waves, 5th Symposium (International) on Combustion, 664-71, Reinhold, New York (1955).

7. G. Skinner, J. Chem. Phys., 31, 268, (1959).

8. J. Hirschfelder and C. Curtiss, J. Chem. Phys., 28, 1130-51, (1958).

Figure 1. (x-t) Schlerien photograph of adiabatic explosion leading to simple acceleration of the reflected wave. Time increases toward the right. Back wall of shock tube at top. Vertical line is stationary slit image. 70% argon, P_o = 1 cm Hg, M_s = 2.76, T_{rs} = 1570°K, delay at back wall is 31.5 microseconds.

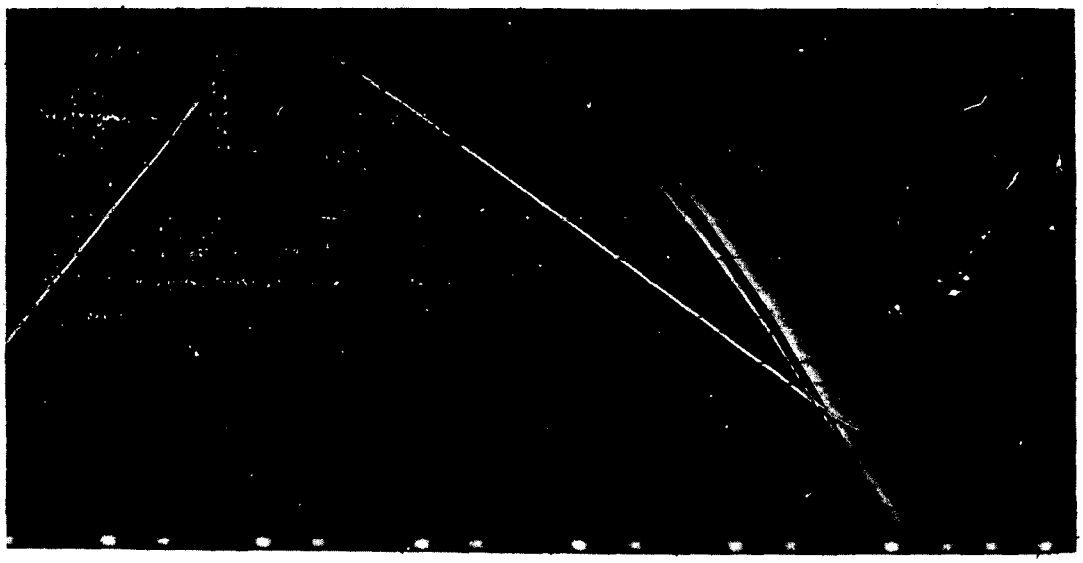

Figure 2. (x-t) Schlerien photograph of the initiation of detonation behind the reflected wave. Notice the interaction of the developing detonation and the reflected wave. Time increases to the right. Back wall of shock tube at top. 85% argon, P_o = 4 cm Hg, M_s = 2.22, T_{rs} = 1160°K, delay at back wall is 135 microseconds.

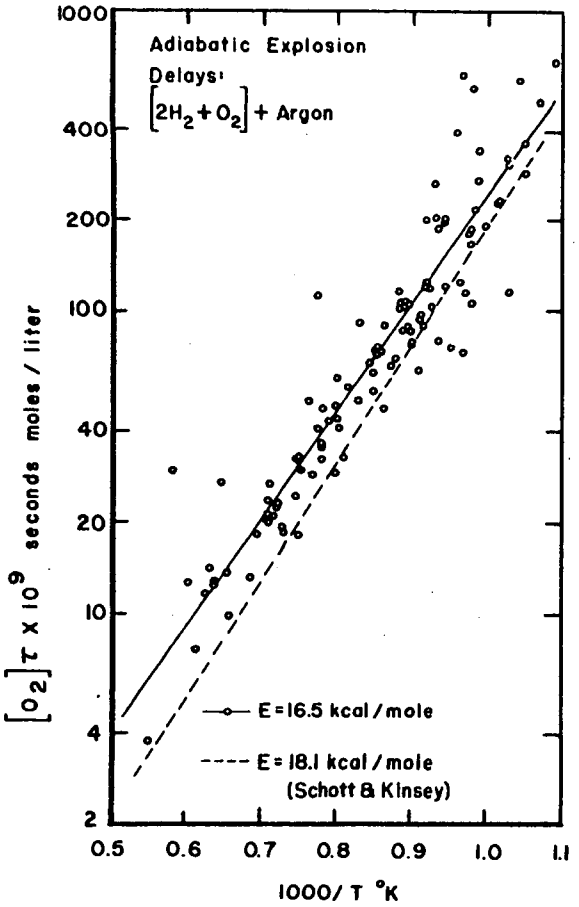

Figure 3. Adiabatic explosion delays measured for stoichiometric hydrogen-oxygen mixtures diluted with argon. Temperatures are calculated from incident shock velocities and one-dimensional theory.

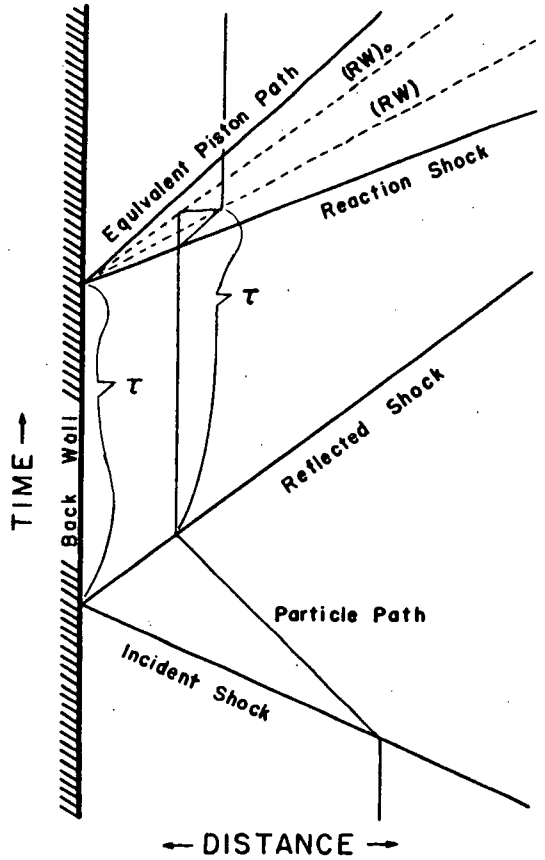

Figure 4. Schematic (x-t) diagram illustrating the mechanism of shock formation for a delayed exothermic reaction occurring behind the reflected shock.